



Solid-State Power Generation and Cooling Micro/Nanodevices for Distributed System Architectures

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by

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 - G. J. Snyder, C.-K. Huang, M.A. Ryan, J. A. Herman, A. Borshchevsky, R. Williams and T. Caillat Thermal Design Group

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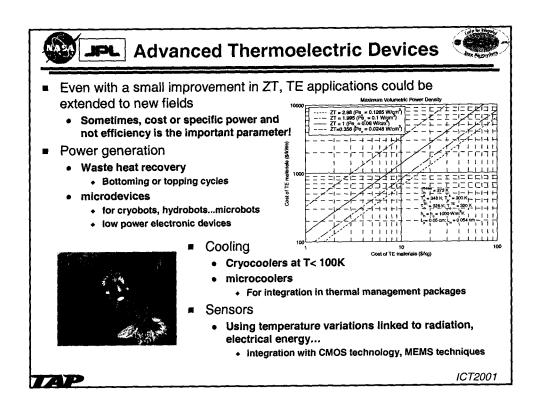
- E. Kolawa
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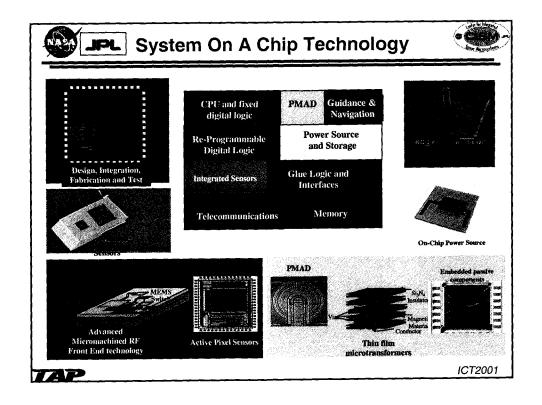
MIT. UC Berkeley, Howard University, UC Santa Barbara

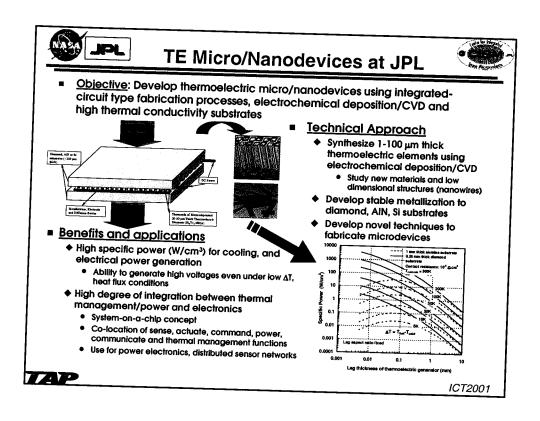
M. Dresselhaus, A. Stacy, T. Huber, G. Stucky

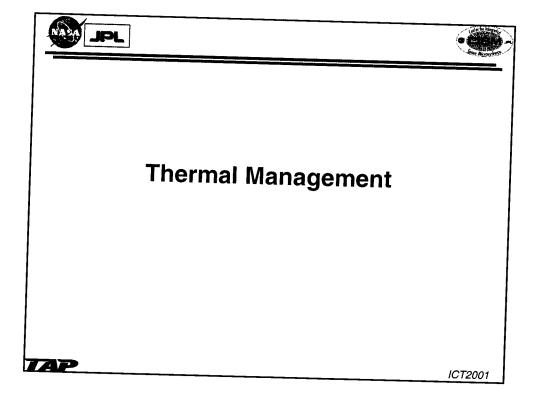
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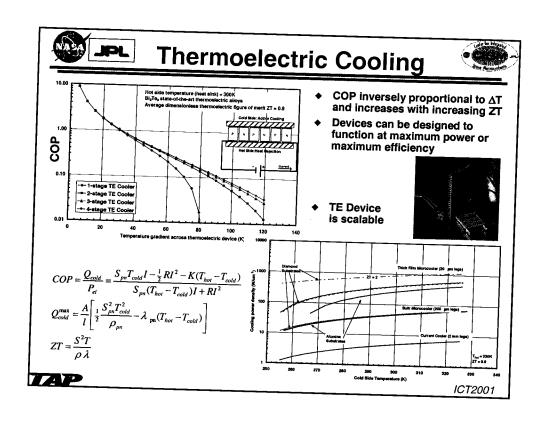
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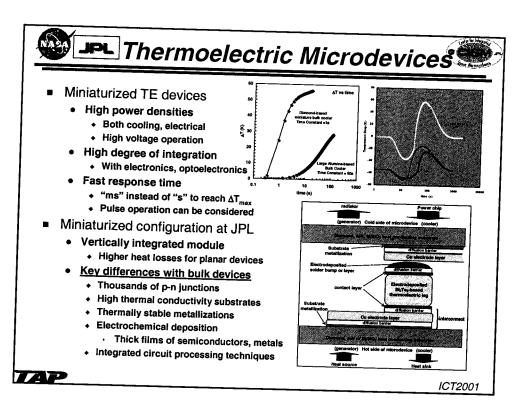


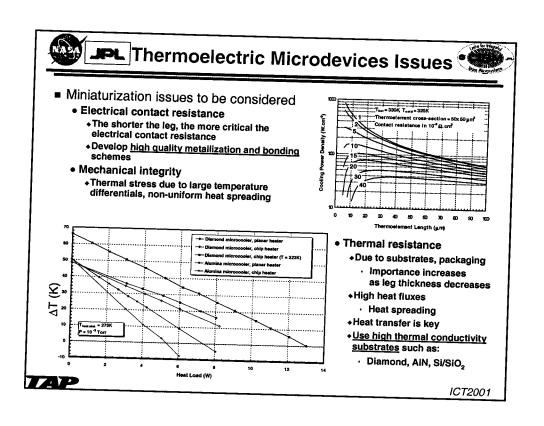


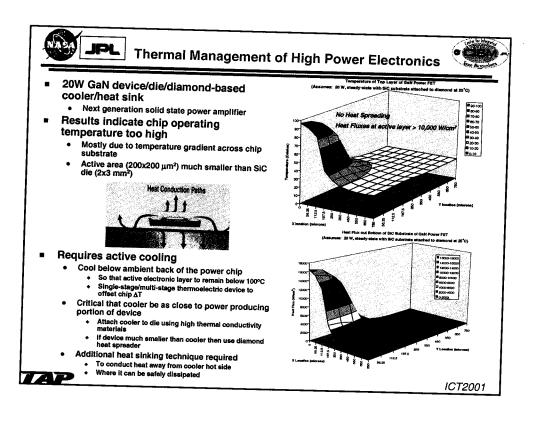


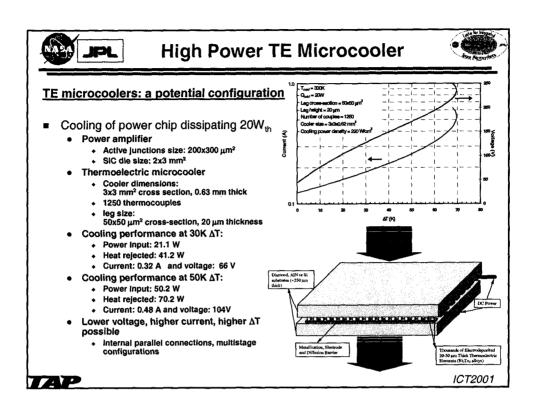


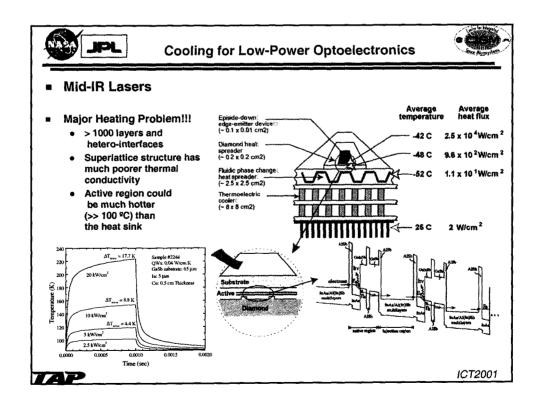


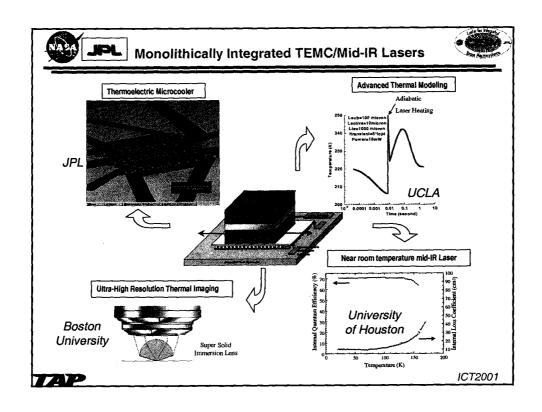


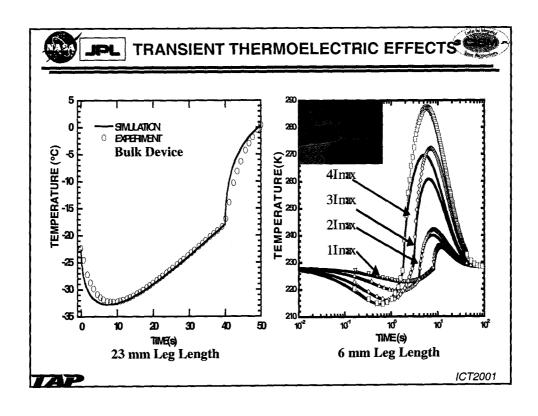


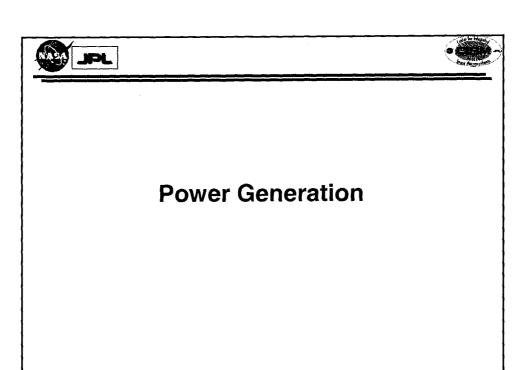




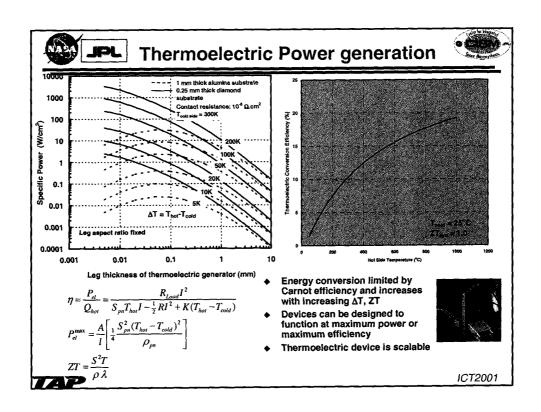


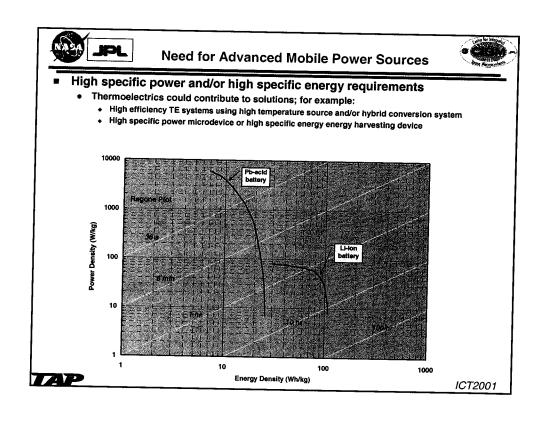


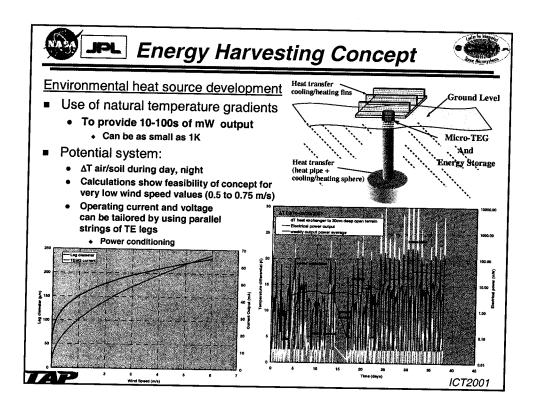


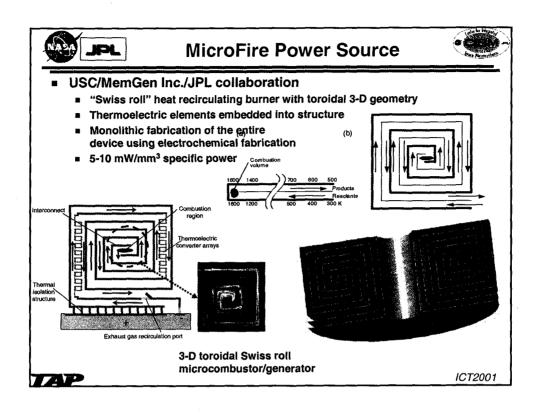


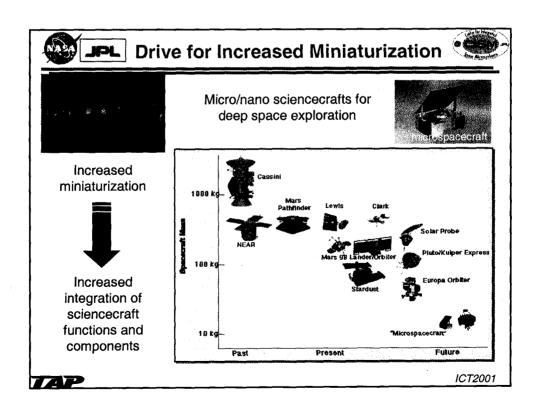
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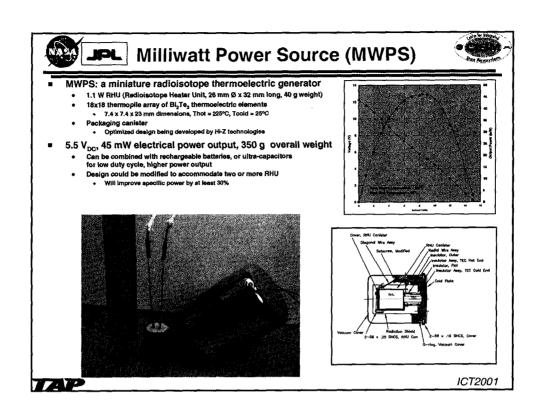


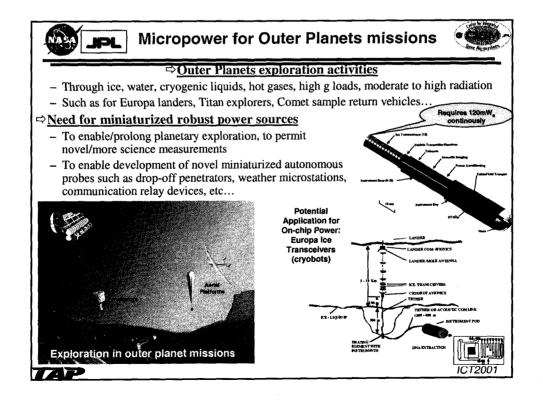


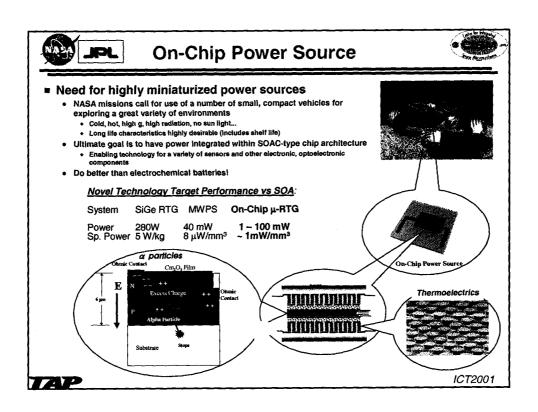


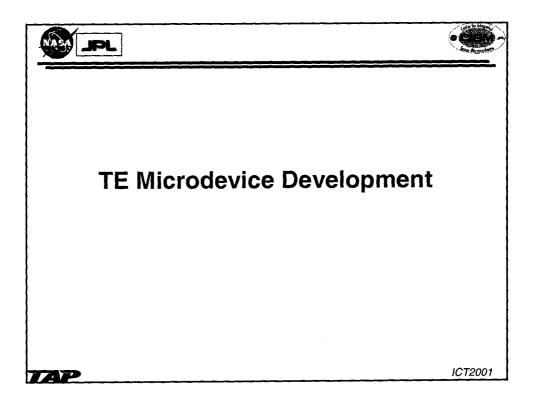










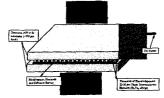


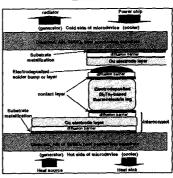


Electrochemical Deposition for Thermoelectric Microdevices



- Key challenges for TE microdevice fabrication
- Electrochemistry
 - n-type and p-type Bi_{2-x}Sb_xTe₃ deposition
 - Optimization of thermoelectric properties
 - Morphology and stress control of semiconducting and metallic electrodeposits
- Photoresist (PR):
 - High aspect ratio patterns in up to 75 μm thick PR
 - . Multiple processing of PR layers
 - · Post-fabrication removal of processed thick PR layers
- Legs and interconnects
 - Adhesion between metal and semiconductor layers
 - Removal of metallic layers without damage to semiconductors
 - Alignment between multiple fabrication steps
 - Mechanical strength and resistance to high temperature anneals





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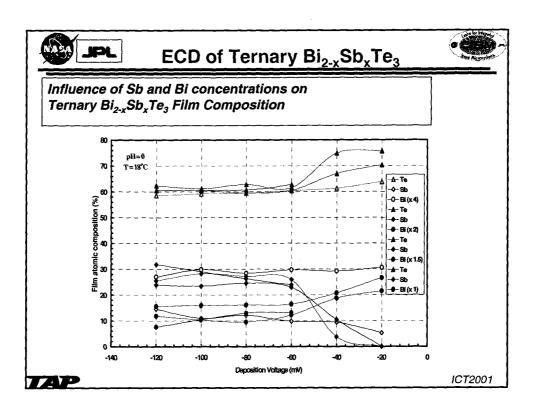




- An attractive route to deposition of thick films of TE materials
 - High deposition rate on metallic substrates
 - Room temperature process, inexpensive, and scalable
- Bi_{2-x}Sb_xTe_{3-y}Se_y deposition
 - $13H^+ + 18e^- + 2BiO^+ + 3HTeO_2^+ \rightarrow Bi_2Te_3 \downarrow + 8H_2O$
 - JPL using potentiostatic control
 - Manual, computer-controlled equipment
 - Many process parameters
 - Deposition voltage, current
 [Bi] concentration, [Bi]/[Te] ratio...
 - Deposition setup, stirring rate, substrate quality, pH, temperature
- Deposition of other metallic layers
 - Cu, Nì, Pt, PbSn solder...
- Up to 11,000 legs grown using a 30 μm pitch
 - In 3x3 mm² area
- Process offers tremendous <u>flexibility</u> for configuring microdevices







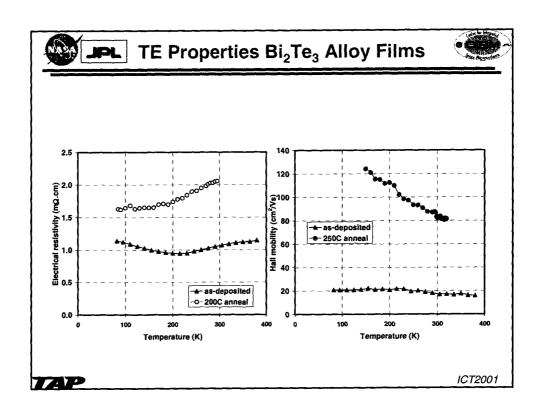


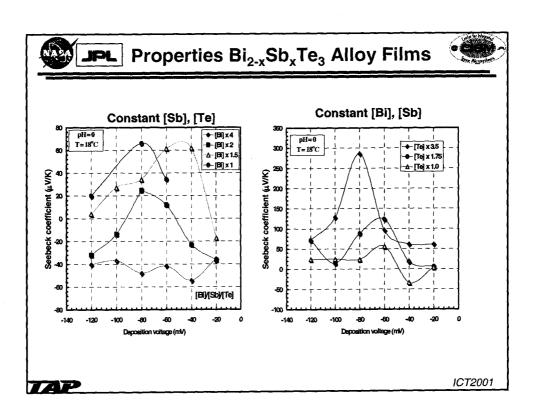
TE Properties Bi₂Te₃ Alloy Films



- As-deposited Bi₂Te_{3-x}Se_x films
 - Show heavily doped n-type behavior
 - S = -40 to -60 μV/K; (cross-plane measurement)
 - + ρ ~ 1 m Ω .cm; n ~ 1x10²⁰ cm⁻³; μ_H ~ 15-25 cm²V⁻¹s⁻¹ (in-plane measurement)
 - $\lambda = 11 \text{ mW/cmK}$;
 - (AC calorimetry in-plane measurement, 3-w measurement underway)
- Electrical properties are improved by anneals
 - Doping levels decrease and carrier mobilities increase
 - S up to -200 μV/K after 250°C anneal
 - + ρ = 2-3 m Ω .cm; μ_H up to 80 cm 2 V $^{-1}$ s $^{-1}$ (in-plane measurement)
- As-deposited Bi_{2-x}Sb_xTe films
 - As deposited: Seebeck values range from -60 to +250 $\mu V/K$
 - Seebeck values highly sensitive to film stoichiometry
 - Excess Te, Bi/Sb atomic ratio
 - Heat treatment study
 - Anneals in 200 to 300°C range improve p-type character of films
 - As for n-type, annealing of defects with donor-like behavior
- More work to be done to complete characterization
 - Film-level and device-level measurements

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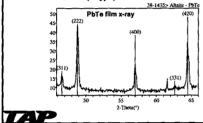


ECD of other TE Materials



CoSb₃ film analysis

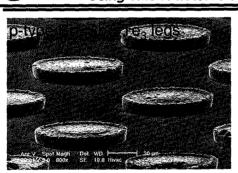
- Exploring practical approaches to the electrodeposition of attractive TE materials for high temperature operation
 - PbTe and its alloys
 - Also PbTe-Bi₂Te₃ based layered compounds
 - Skutterudites such as CoSb₃
- Experimental results to date on PbTe
 - Also using acidic PbTe aqueous solution
 - Pb+Te codeposition in -130 to -400 mV vs. SCE range
 - Both Pb-rich (p-type) and Te-rich (n-type) films obtained



- Experimental results to date on CoSb₃
 - Near neutral Co/Sb aqueous electrolyte at room temperature
 - Chelating agents
 - Codeposition of Co and Sb
 - · From same bath
 - . Some deposition conditions lead to mostly CoSb₃ phase
 - + Characterization under way

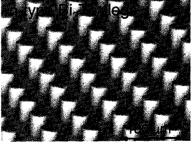
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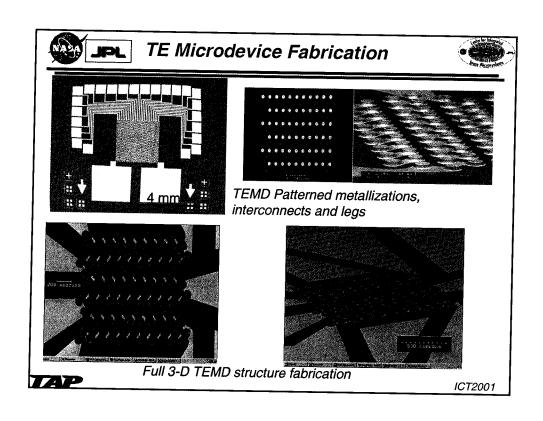
Photoresist template (top)

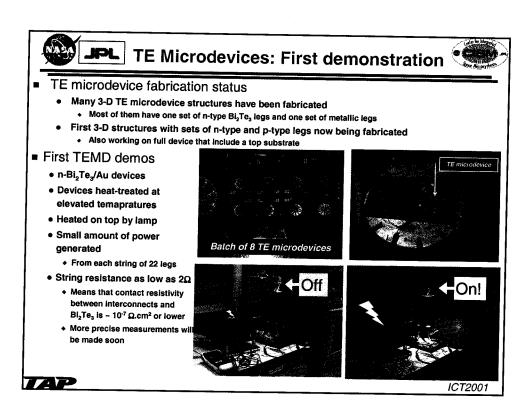


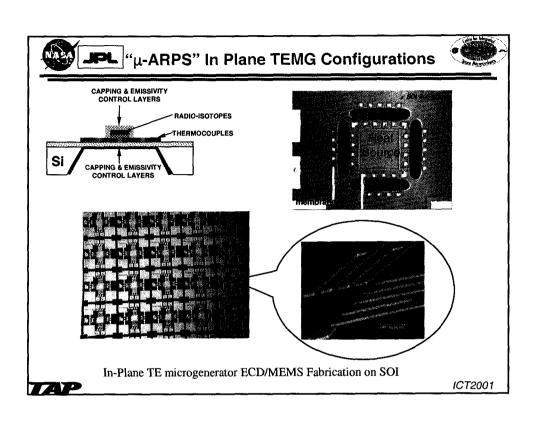


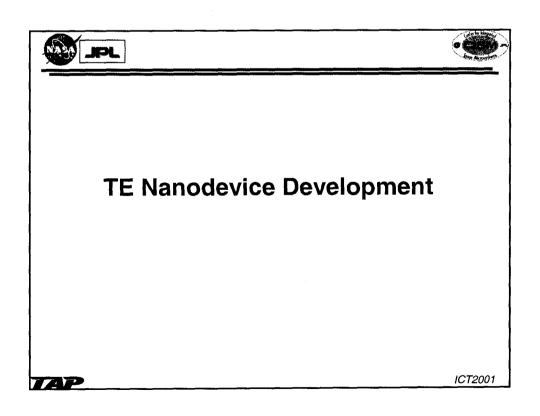
Photoresist template (side)













Nanowire Thermoelectric Generator



- Proof-of-principle microdevice for a high performance microscale nanowire-based thermoelectric generator
 - Nanowires as TE legs with 20 nm diameter and 50 to 60 μm helght
 - + Using anodized alumina templates
 - Using conventional microelectronics processing techniques
 - Quantum confinement, interface scattering could lead to 4-5% efficiency at $\Delta T = 50K$
 - High power density from thousands of legs
 - >> 1000,000 in 1 cm²
 - · Open Circuit Voltage > 100 V for ΔT = 50K
- Experimental results to date
 - Grew n-type Bi₂Te₃ and p- type Bi_{2-x}Sb_xTe₃ nanowires electrochemically
 - Up to 60 μm long
 - Developed methods for processing nanowires
 - Electrodeposited 10-20 nm x 40 μm Bi₂Te₃ elements
 - Conducting studies to make 10 nm alumina templates
 - Measured some thermoelectric characteristics of n-type Bi₂Te₃ wires
 - Seebeck Coefficient as high as -125 μV/K
 - Initiated collaborations with various universities

- For energy harvesting application
 - Energy harvesting of rejected heat in various structures to increase overall efficiency, autonomy
 - Rejected heat on solar arrays, small spacecraft
 - Power for microdevices
 - High voltage even with small ΔT
 - Power for science instruments, sensors, SOAC
 - + Other waste heat recovery applications



Nanowire-based, small AT, high voltage microgenerator (concept)





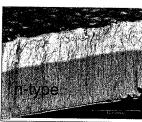
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Electrodeposition into Nanostructured Templates

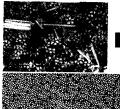


■ Both n-type and p-type Bi_{2-x}Sb_xTe₃ nanowires





 Polished top surface of Bi₂Te₃ nanowires filling an anodized alumina template









TEMDs: Summary



- Many applications available if thermoelectric microdevices can successfully demonstrate predicted performance
- Waste heat recovery and spot cooling are promising areas
 - Microgenerators and microcoolers for integration with electronics

 New technology based on electrochemistry of SOA materials

 - · Batch fabrication possible
 - Technology and lessons learned could later be used for application of low dimensional structures in TE devices
- SOAC-like technical approach for use of TE micro/nanodevices
 - Distributed architecture for power thermal management where it is needed
 - . Enhanced autonomy, reliability
 - . Modular, scalable technology: ECD, CVD, IC, MEMS
 - Embedded, rugged power sources:
 - · Waste heat, energy harvesting, combustion, radioisotope heat sources
 - High specific power could be possible: mW/mm³ capability
 - Hybrid conversion and conversion/storage solid-state systems
 - Integrated cooling/thermal management
 - . Cooling device fabrication and integration technology compatible with electronics/optolectronics
 - · Hybrid cooling technologies

